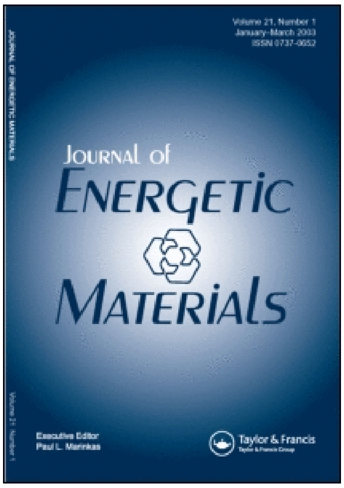

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Initiation mechanism of TNT: Deuterium isotope effect as an experimental probe

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INITIATION MECHANISM OF TNT: DEUTERIUM ISOTOPE EFFECT AS AN EXPERIMENTAL PROBE

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ABSTRACT

A large deuterium kinetic isotope effect in the thermal decomposition of methyl deuterated 2,4,6-trinitrotoluene (TNT-α-d_3) has been confirmed and tested for its possible influence on the shock sensitivity and detonation velocity. A comparison of the exploding foil shock sensitivity tests and miniature detonation velocity measurements performed on TNT-α-d_3 and two differently prepared control samples of unlabeled TNT showed that the former was significantly lower in sensitivity as well as detonation velocity. These results indicate that the rate-determining steps in the controlled condensed phase decomposition and in the chemical mechanism of initiation and detonation are likely to be the same.

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INTRODUCTION

The precise chemical steps involved in the initiation of an explosive to detonation have always defied direct experimental study due to the inherently violent nature of the process[1]. Models for detonation chemistry, therefore, have been generally based upon observations of milder degradative methods such as thermal decomposition[1,2]. One such example is the recent study of the thermochemical decomposition of liquid TNT (2,4,6-trinitrotoluene) by Shackelford[3] et al in which the rate determining step was identified as the methyl C-H cleavage by a primary deuterium isotope effect in the methyl-deuterated (TNT-α-d_3) sample. While it represents an elegant method to recognize the rate-determining step in the otherwise complex chemistry of TNT decomposition, it raises the question of the relationship of this mechanism to the initiation process of TNT. The present work is an attempt to answer this question by an extension of the diagnostic isotope effect study to the explosive properties. Preliminary results illustrating this novel approach with methyl-deuterated TNT are reported here. Two parameters representing the detonation process, namely, shock sensitivity and detonation velocity of TNT-α-d_3 were determined. A decrease in both parameters was observed relative to two different control samples of normal TNT suggesting an influence of deuterium kinetic isotope effect in the rate-controlling step on the initiation process.

EXPERIMENTAL

Test Samples

TNT-α-d_3 (TNT-2) was obtained in 80% yield by nitration[4] of toluene-α-d_3 with HNO_3 and H_2SO_4 and was recrystallized from 95% ethyl alcohol. Two different control samples, TNT-1 and TNT-3, were prepared by recrystallizing military grade sulfite treated and untreated samples, respectively, from 95% ethyl alcohol. All three samples had similar particle size distribution (average particle size: 390-460 microns; 85% of crystals were between 100-1000 microns in size) and gave the same m.p. (82°C). The TNT-α-d_3 was found by mass spectrometry to be 97.5% isotopically pure.

Shock Sensitivity

The shock sensitivity of each sample was determined by the exploding foil method often employed in this laboratory and described in detail in the literature[5,6]. Briefly, the method consists in applying incremental high voltage, high current pulses from a capacitor to 1 mil aluminum foil which instantly vaporizes. The expanding gas from this drives a 2-mil mylar flyer film to impact the explosive sample pressed into a steel washer to a known density, constant in a given series of tests. A steel witness disk is used to determine if the sample has detonated. This test was performed on the three samples of TNT in the order, TNT-1, TNT-2, and TNT-3 with the middle one being TNT-α-d_3 in order to avoid systematic errors. The results are summarized in Table-1 and it should be noted that higher flyer velocities correspond to lower sensitivities.

Miniature Detonation Velocity Test

The principles and details of the standard detonation velocity tests of explosives are described elsewhere in the literature[7]. In the present miniature tests[8] samples of TNT were pressed into 0.2" dia. x 0.375" long pellets at a pressure of 11,000 psi (density, 1.5 g/cc) and loaded into brass tubes 0.201" i.d. x 1" o.d. x 1.5" long. Six ionization velocity pins were spaced 0.15" apart and inserted through holes drilled on the sides of the brass tubes. The pin distances were measured by a travelling microscope accurate to 0.0001 inch. The propagation time of the detonation wave (initiated by a Reynolds PE-2 EBW detonator[8]) was measured by a Biomation 8100 transient digital recorder.

Table-1. Miniature Detonation Velocity and Exploding Foil Shock Sensitivity Measurements of TNT-1, TNT-2 (TNT-α-d_3), and TNT-3

Sample	Detonation Velocity[a] (mm/μsec)	Shock Sensitivity[b] (Flyer Velocity for 50% Fire) (Based on 25 tests each) (mm/μsec)	Std. Dev.
TNT-1 (control)	6.371	3.381	0.127
TNT-2 (TNT-α-d_3)	6.145	3.681	0.155
TNT-3 (control)	6.491	3.237	0.170

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[a] Densities of pellets, 1.5 ± 0.01 g/cc; error limit, in velocity measurement = 0.008 mm/μsec.

[b] Density of pressed samples, 1.54 g/cc (50 mg ea.); standard deviation estimated by Bruceton Method[9].

RESULTS AND DISCUSSION

The existence of kinetic isotope effect in the thermal decomposition of TNT-α-d_3 was first confirmed by a differential scanning calorimetry experiment in which the decomposition exotherm appeared 24° higher than for normal TNT at a heating rate of 10°/min. The shock sensitivity and detonation velocity values for TNT-2 (TNT-α-d_3), shown in Table-1, indicate a small but definite decrease relative to the control samples. For example, the order of magnitude of the difference in sensitivity is the same as that between Class A RDX, Comp B, and PETN[5]. It is, therefore, considered that this difference in sensitivity represents a significant trend even though small in magnitude, and a parallel drop in detonation velocity further supports this conclusion.

If the primary bond-breaking steps of the shock initiation process are the same as in the slow thermal decomposition, one would intuitively expect a drop in sensitivity due to the primary deuterium isotope effect on the rate controlling step. The complex nature of the detonation chemistry precludes a quantitative estimate of change in sensitivity based on the kinetic isotope effect. The detonation velocity of TNT-α-d_3 was compared with that of the normal TNT on the assumption that it is a function of the rate of release of energy which in turn is dependent on the rate of the critical reactions subject to kinetic isotope effect. The trend here also suggests an isotope effect and a slowing down of the overall rate of reaction which drives the detonation.

The proximity of the CH_3 amd NO_2 groups in TNT causes a hydrogen rearrangement ("ortho-effect") in the photochemical[10] and electron impact[11] decomposition giving the aci-nitro isomer and the $(M-OH)^+$ ion, respectively. Evidence was also found by ESCA study[12] for a hydrogen rearrangement in the TNT photolysis. Formation of 4,6-dinitroanthranil and 2,4,6-trinitrobenzylalcohol among the condensed phase thermal decomposition products[13] also clearly indicates a similar step. The primary kinetic isotope effect, observed in both the decay and the induction period kinetics of the same by Shackelford[3] et al, strongly suggests that benzylic C-H bond rupture was the critical rate-determining step. The same work also revealed an unidentified product during the induction period having a profound catalytic effect on the rate.

The present work on shock initiation of TNT-α-d_3 suggests that the same benzylic C-H rupture is likely to be the rate determining step in the chemistry of the initiation process. Further confirmation of this similarity is being sought in the work currently in progress by attempting to detect and identify any possible catalytic product or an intermediate radical species from the C-H bond rupture under a sub-initiation threshold shock. However, the observed deuterium kinetic isotope effect on the shock sensitivity and detonation velocity of TNT does indicate an essential similarity of the fast reaction mechanisms under the influence of a shock to those of controlled thermal decomposition in the condensed phase. In contrast, it is interesting to note that, in their work on gas phase laser-powered homogeneous pyrolysis of o-nitrotoluene and other ortho-substituted aromatic nitro compounds, Lewis, McMillen, and Golden[14] found that the kinetics correspond to a predominant C-NO_2 bond scission.

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Note Added in Proof: We thank a referee for pointing out our omission of reference to a paper on TATB by Rogers, et al[15] in which deuterium isotope effect was effectively used for objectives similar to ours.